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Process for the preparation of dentures

The invention relates to a process for the preparation of dentures. Furthermore the invention relates to pre-sintered blanks of zirconium oxide ceramic which have a raw breaking resistance in a selected range.

Ceramic dentures are normally prepared by grinding of densely sintered ceramic blanks.

Thus in EP-B-O 160 797 for example a blank and its use for the preparation of dental shaped parts using a grinding tool is described. Furthermore a process for the preparation of ceramic dental prostheses is known from EP-A-0 630 622 in which a blank of a certain composition is ground using a rotating tool.

A disadvantage of the processing of densely sintered blanks is in particular their high hardness which leads to long processing times and high wear of tools. The costs of the processing of these blanks are thereby very high.

A disadvantage of grinding processes for the processing or preparation of ceramic dentures is furthermore that a high-precision shape of the ground blanks cannot be ensured due to the lack of defined cutting edges.

The processing of blanks pre-sintered to a certain degree of hardness is mentioned in principle in EP-A-O 630 622 on page 3, column 3, lines 13 ff., but the processing of the blanks by grinding processes is retained.

Pre-sintered blanks have a lower hardness than those which are densely sintered and show a higher hardness than those which are not sintered. It is therefore desirable in principle, in order to guarantee easy processing or to first make processing possible, to use pre-sintered blanks.

Thus for example the processing tools are less severely worn, which leads to longer service lives of the tools and thus to considerably reduced costs. The preparation of very fine microstructures also first becomes possible as the predictable shrinkage of the ceramic during dense sintering leads to a further reduction in size of the produced microstructures. The frequent microscopic damage to the ceramic during processing can be cured in the case of pre-sintered blanks within the framework of the dense sintering process.

In order to be able to prepare dentures by processing in the non-densely sintered state, a completely homogeneous distribution of the strength and hardness and the density within each spatial direction of the ceramic blank is necessary, which in particular is also retained after the pre-sintering of the blank. It is advantageous to avoid deviations in the density and hardness distribution of the ceramic when filigree structures or multi-section bridges are to be prepared, as even the slightest inhomogeneities can lead to breaking points which considerably impair the durability of these complex structures during the processing or can lead to a different sintering behaviour, behaviour which can be recognized from the distortion of the workpiece during sintering. Such a distortion leads however to poor fitting accuracy and thus to unusability of the denture.

For the following reasons the processing of pre-sintered blanks has up until now not led to a technical realisation:

The dense sintering of a pre-sintered blank after processing is associated with changes in dimensions which are difficult to calculate and can be applied to the actual milling parameters only by means of complicated processes. Thus subsequent adjustments are necessary on non-accurately-fitting denture parts after dense sintering. Due to the higher hardness of the densely sintered denture parts these have to take place using removal processes and are to be evaluated as very critical, as a self-healing of injuries to the surface structures, such as takes place during the dense sintering process, can no longer be made good.

In summary, there is a considerable demand for methods for the preparation of accurately-fitting dentures using pre-sintered ceramic blanks.

It is therefore the object of the invention to make available an improved process for the preparation of accurately-fitting, highly-precise dentures.

Surprisingly this object can be achieved by a process for the preparation of dentures, comprising the steps:

a) preparation of a blank,
b) processing of the blank by milling methods,
c) dense sintering of the blank in a temperature range from 1200 to 1650°C,

the blank comprising a pre-sintered material and having a raw breaking resistance of 15 to 30 MPa, preferably 23 to 28 MPa.

By blanks is meant within the framework of this invention a non-processed material block or moulding which is subsequently passed to a shaping stage through the processing. These blanks can consist of the most varied materials, in particular ceramics.

By dentures are meant within the framework of this invention in particular crowns and bridges having three or more sections. The blanks according to the invention are particularly suitable for the preparation of bridges having three or more sections.

By processing is meant within the framework of this invention milling measures for shaping a blank, which lead to the blank being converted into a shape coming as close as possible to a natural tooth. Not meant by processing is cleaning of the blank processed in the above sense or the removal of support and holding

structures which result from the embedding of the blank in a blank holder, even if this cleaning can be carried out by milling methods.

The terms "comprise" and "containing" within the meaning of the present invention introduce a non-limitative list of features.

Customary raw breaking resistances known from the state of the art for ceramic dental blanks are in the higher strength range, for example from 75 to 110 MPa; such blanks cannot be used for the invention.

It was found that the processing of pre-sintered blanks, the raw breaking resistance of which lies outside the range according to the invention, does not lead to usable results. In the case of lower raw breaking resistances, the resulting blanks are too soft, and can fracture during milling, whereas in the case of higher raw breaking resistances the resulting blanks are too hard, and neither can be processed with the normal processing procedures.

The processing of the blanks pre-sintered according to the invention is carried out with milling methods. Very fine microstructures can be produced by the extremely sharp cutting edges of the milling tools. The cutting edges of the tool remain sharp over a long use period, as the blank in its pre-sintered state has only a low hardness and strength. During the milling of the blank the tool of the processing machine operates during rough working for example at a speed of 5,000 to 40,000 rpm, preferably 15,000 to 25,000 rpm with a feed rate of 20 to 5,000 mm/min, preferably 500 to 3,500 mm/min. The fine processing takes place for example at a speed of 5,000 to 50,000 rpm, preferably 18,000 to 35,000 rpm with a feed rate of 20 to 5,000 mm/min, preferably 500 to 3,500 mm/min. In both processing steps a milling diameter of 0.8 to 4 mm is used for example.

The blanks are particularly preferably processed without a supporting structure as described for example in the example of EP-A2-0 824 897. The processing

step takes place from the side of the fully processed denture part in contact with the tooth stump and from the side not in contact with the tooth stump. It is of particular advantage that the blank need not be surrounded or supported by a high-temperature investment compound during the dense sintering process.

During the course of the dense sintering process, the processed blank can be held by means of carrier devices which adapt independently to the contraction dimensions occurring during the baking process, such as are known for example from the patent application DE-199 04 534, to avoid a distortion during the sintering process.

The blanks can consist of normal dental ceramics. By dental ceramics are meant within the framework of this invention compositions which, along with the normal ceramic constituents, can also optionally contain small amounts of other constituents (additives), such as sintering auxiliaries. Data relating to formulations in the form of components and wt.-% always relates to a product which no longer contains additives. Small traces of additives, also in the pre- or post-sintered ceramics are of course also possible for kinetic, thermodynamic or chemical reasons and are therefore to be understood as also contained within the scope of protection of this invention.

In particular the presence of impurities encourages the formation of glass phases or glass. Blanks which do not form any glass phases or glass during the dense sintering are therefore preferred.

The blanks according to the invention furthermore display a preferred deviation from the linearity of the shrinkage per spatial direction which is less than 0.05 %, particularly preferably less than 0.01 %.

The blanks according to the invention preferably consist of aluminium oxide or zirconium oxide ceramic. Zirconium oxide ceramic is particularly preferred.

It is known that the strength of nonmetallic-inorganic systems in general depends on the critical stress intensity factor K_{IC}. This factor is clearly lower with amorphous materials, for example glasses, than with purely crystalline systems (D. Munz/T. Fett: Mechanisches Verhalten keramischer Werkstoffe [Mechanical Behaviour of Ceramic Materials], Springer-Verlag). Thus the strength of ceramics also decreases if amorphous phases form at the grain boundaries. The ceramics preferably usable according to the invention therefore display for example a K_{IC} value of 5 to 10, preferably 8 to 10, measured according to EN 843.

Surprisingly it was ascertained that ceramics based on zirconium oxide with a sinter addition of 0.1 to 0.50 wt.-% of at least one of the oxides of the elements aluminium, gallium, germanium, indium have a particularly favourable and uniformly distributed hardness and strength. They are therefore particularly suitable for the preparation according to the invention of complex dentures and filigree structures. It is an advantage if the oxides of the abovementioned elements are added in an amount as defined above with homogenous distribution and these are not, like say impurities, distributed non-uniformly and with varying concentration. This homogeneous distribution can be achieved for example by co-precipitation as is described in the embodiment of this invention.

In addition a uniform distribution of the particles formed during the pre-sintering process is an advantage. The granular form of the particles is preferably equiaxial with an average grain diameter less than 1 µm, particularly preferably less than 0.7 µm.

The blanks used for the invention normally have a pore volume of 50 to 65 %. The average pore size is normally in the range from 3 µm to 0.1 µm, the range preferably being from 2 µm to 0.2 µm.

In the case of this ceramic, the pre-sintering process is carried out in a preferred temperature range of 850°C to 1000°C, particularly preferably between 950°C and 995°C, in order to achieve the raw breaking resistance according to the invention. The pre-sintering process is carried out for example over a time period of 30 to 55 hours.

Such ceramic systems are known to have a tendency to shrink anisotropically, i.e. have a shrinkage which is different in the three spatial directions. As this shrinkage is linear in itself in each spatial direction, these ceramics are surprisingly extremely suitable for the preparation of extremely accurately-fitting and complex dentures.

The use of zirconium oxide ceramics in the medical field is generally known. Pure zirconium oxide cannot be used for mechanical applications as its volume changes too much through modification changes during the cooling process after sintering. Through the addition of magnesium, cerium or yttrium oxides, however, this process can be checked. A detailed discussion can be found in "Aluminium- und Zirkonoxidkeramik in der Medizin" [Aluminium and Zirconium Oxide Ceramics in Medicine], reprint from Industrie Diamanten Rundschau, IDR 2/1993 and also in EP-A-0 634 149.

The addition of 0.1 to 0.50 wt.-%, preferably 0.15 to 0.50 wt.-%, particularly preferably 0.20 to 0.50 wt.-%, quite particularly preferably 0.25 to 0.50 wt.-% of at least one of the oxides of the elements aluminium, gallium, germanium, indium to such ceramics leads to the lowering of the sintering temperature and the increasing of the stability and the hydrolytic resistance during use. This situation can also be found for aluminium oxide in "Zirconia Powder" 09/97, product information from the company Tosoh. The ceramic is however not suitable for the preparation of accurately-fitting dentures according to the present invention, as without the maintenance of the raw breaking resistance according to the

invention, milling to form highly-accurate dentures is not possible due to the previously discussed effects.

Likewise a subject of the present invention is a pre-sintered blank made from zirconium oxide ceramics of the composition (1), containing:

(A) 91 to 98.45 wt.-%, preferably 91 to 97.25 wt.-% zirconium oxide,
(B) 0 to 3.5 wt.-%, preferably 0 to 2.5 wt.-% hafnium oxide,
(C) 1.5 to 6.0 wt.-%, preferably 2.5 to 6.0 wt.-% yttrium oxide,
(D) 0.05 to 0.50 wt.-%, preferably 0.15 to 0.50 wt.-%, particularly preferably 0.20 to 0.50 wt.-%, quite particularly preferably 0.25 to 0.50 wt.-% of at least one of the oxides of the elements aluminium, gallium, germanium, indium,
(E) 0 to 1.9 wt.-%, preferably 0.0005 to 1.5 wt.-% coloring additives,

the wt.-% having to add up to 100 and the blank having a raw breaking resistance of 15 to 30 MPa, preferably 23 to 28 MPa.

By component (E) of the composition (1) are meant coloring oxides from elements of the group Pr, Er, Fe, Co, Ni, Ti, V, Cr, Cu, Mn, with Fe_2O_3, Er_2O_3 or MnO_2 preferably being used.

A further subject of the invention is a process for the preparation of ceramic dentures, a blank of the composition (1) being processed by suitable processing measures into a shrinkage-matched enlarged model of the end denture and then densely sintered to its end dimensions. By shrinkage-matched model is meant a model of the desired denture enlarged according to part of the theoretically expected shrinkage.

The composition (1) according to the invention is industrially prepared by dissolving the components (A) and (B) of the composition (1) contained in

commercially available zirconium sand with HCl, mechanically separating the low-soluble impurities and combining them with the additives (C) and (D) likewise present as oxichlorides or chlorides after treatment with HCl as an aqueous, strongly acid solution.

Additives according to component (E) acting as colorants are then added likewise as chlorides, obtained through dissolution in HCl.

There follows a co-precipitation of the dissolved components by hydrolysis, calcination of the precipitation product, grinding of the calcinate to the desired end fineness and also a spray-drying process using temporary slip and binding agents.

The thus-obtained granules can be converted into the desired preform with known compression processes. These compressed blanks are separated by a binder-dependent heat treatment and pre-sintered at a temperature between 850°C and 1000°C, preferably between 950°C and 995°C, for example with 0.5 to 4 h holding time.

Ceramic powders containing the components (A) to (D) are also commercially available (Tosoh, Tokyo, Japan).

The blanks processed with customary processes, for example CAD/CAM or copy-milling, are densely sintered at 1200°C to 1650°C, particularly preferably 1350°C to 1550°C, for example with 1 to 3 h holding time.

Preferably before the dense sintering, aesthetic measures such as individual coloring can be carried out. Usable are for example processes according to the patent application DE-199 04 522, the use of ionic solutions of at least one of the salts of the rare earth elements, of the lanthanides or the elements of the group Fe, Co, Ni, Ti, V, Cr, Cu, Mn being preferred.

Optionally, after dense sintering, the ceramic blanks processed to form a dental prosthesis are removed from a blank-holding device, a holding device from the utility model DE-298 154 86 for example being able to be used during processing. After the removal from a blank-holding device, the blank can optionally be re-processed for the purpose of removing holding pins or connection points between the blank-holding device and the processed blank.

Furthermore, the blank can be faced using customary measures. For this purpose, a facing compound which has the same coefficient of thermal expansion as the blank can be burned onto the blank. Blanks which are suitable for the present invention can for example have a coefficient of thermal expansion between 9.0 and 10.5 ppm/K, preferably between 9.4 and 9.8 ppm/K.

The invention is explained in more detail in the following by means of examples without thereby being limited in any way.

Strength data, in particular breaking resistances within the framework of these statements, relate to the "piston-on-three-ball test" according to ISO 6872.

To prepare the blanks according to the invention, preforms obtained while applying pressure are taken as a basis. When preparing these preforms, examples of starting materials are pure chlorides, oxichlorides or nitrates, chlorides being used in the examples.

Preparation examples 1 and 2

Zirconium oxide ceramic containing aluminium oxide

To obtain approx. 200 g of ready doped compressed granules, the components are dissolved in distilled water according to the following table:

No.	$M(ZrCl_4)$ [g]	$M(YCl_3 \cdot 6H_2O)$ [g]	$M(AlCl_3)$ [g]	$M(FeCl_3)$ [g]	$M(ErCl_3)$ [g]
1 [coloured] (% as oxide)	355.6 (94.0)	33.4 (5.17)	0.65 (0.25)	0.77 (0.2)	0.29 (0.38)
2 [uncoloured] (% as oxide)	357.66 (94.55)	33.36 (5.20)	0.65 (0.25)	0	0
Component	(A)	(C)	(D)	(E)	(E)

There follows a co-precipitation of the dissolved components by hydrolysis, the aforementioned solution being reacted with 32 l 6-molar aqueous NH_4OH solution. An at least 30-times excess of OH^- concentration relative to the stochiometric requirement is recommended. The precipitation product must then be washed free of Cl^-. The calcination of the precipitation product is carried out at 700°C over 0.75 hours, followed by a grinding of the calcinate to an end fineness of D_{50} = 0.6 µm and also by a spray-drying process using temporary slip and binding agents (here: 2.0 wt.-% PVA, 0.15 wt.-% oleic acid relative to oxide).

Using an isostatic press, for example at 1500 to 2500, preferably 1700 to 2200 bar, the granules obtained are made into preforms measuring d = 31 mm and l = 150 mm.

The preforms are released from the binder by a heat treatment (heating rate: 4 K/min to 650°C, 1 hour holding time) and pre-sintered at a temperature of 970°

with 0.5 hours holding time to produce the blanks that can be used according to the invention.

Process examples

To prepare accurately-fitting bridges, blanks prepared according to the preparation examples 1 and/or 2 are worked with a CAD/CAM system by milling and densely sintered under the following parameters:

Heating rate: 10 K/min to end temperature: 1500°C
Holding time at end temperature: 2 h

The result is in both cases extremely accurately-fitting dentures with a high strength (σ > 1000 MPa).